

MERCURY PATHWAYS IN MUNICIPAL WASTEWATER TREATMENT PLANTS

S. BALOGH¹ and L. LIANG²

¹ Research and Development Division, Metropolitan Waste Control Commission, 2400 Childs Road, St. Paul, MN, 55106 USA, ² Brooks Rand, Ltd, 3950 6th Avenue NW, Seattle, WA, 98107 USA

Abstract. A nine-week sampling and analysis program was completed at a large municipal wastewater treatment plant to characterize the fate of Hg entering the plant. Mercury removal in primary treatment averaged 79%, and the average Hg removal across the entire plant was approximately 96%. Mercury loadings on the secondary (activated sludge) treatment process were elevated to near plant influent levels due to the recycle of spent scrubber water from sewage sludge incinerator emissions control equipment. This internal recycle of spent incinerator scrubber water resulted in elevated Hg loadings to the incinerators, and effectively reduced the Hg control efficiency of the emissions control equipment to near zero. Measurements indicate that approximately 95% of the Hg mass entering the plant is discharged to the atmosphere via sludge incinerator emissions. These results indicate that municipal wastewater treatment facilities can remove Hg from wastewater quite effectively; however, where wastewater sludge is incinerated, almost the entire mass of Hg removed from the wastewater can be discharged to the atmosphere.

1. Introduction

Municipal wastewater treatment plants represent the focusing point of modern society's industrial, commercial and domestic liquid wastes. Although treatment plants are designed for BOD and solids removal, they are facing ever more stringent expectations with respect to their removal of heavy metal and synthetic organic pollutants. To the extent that heavy metals are associated with particulate phases, removal with solids is generally good; dissolved species represent more of a problem (Oliver and Cosgrove, 1974; Lester *et al.*, 1979; Stoveland *et al.*, 1979). In the case of mercury (Hg), good liquid-side removals are typically observed, and discharges to receiving waters are minimized (Oliver and Cosgrove, 1974; Goldstone *et al.*, 1990). The removal of Hg from wastewater prior to discharge to receiving waters is necessary to protect those waters; equally important is the ultimate immobilization of the Hg removed. Where sewage solids are incinerated, Hg can be released to the atmosphere, and ultimately deposited in the environment. It has been estimated that Hg discharged to the atmosphere can reside there for months, and it is now clear that atmospheric Hg emissions can result in deposition on local, regional and global scales (Lindqvist and Rodhe, 1985). Mercury deposition and transport to lakes has resulted in fish consumption advisories across North America and northern Europe (Lindqvist *et al.*, 1991; Swain *et al.*, 1992). Elevated Hg levels in fish can represent a threat to the health of sensitive human and animal populations which consume the fish (Clarkson, 1990; Minnesota Pollution Control Agency, 1992a). Chlor-alkali plants, metals smelting and processing, fossil fuel combustion and waste incineration have been identified as major anthropogenic contributors to atmospheric Hg loadings (Lindqvist *et al.*, 1991). Based on recent data, sewage sludge incineration in the United States probably accounts for no more than 3000 kg/year in Hg emissions (EPA, 1990). However, emissions from particularly

large sewage sludge incineration facilities may exceed those from all but the largest power and waste incineration facilities (Minnesota Pollution Control Agency, 1992b). In order to better understand, and ultimately reduce, the contributions of municipal wastewater treatment plants to environmental Hg loadings, this study undertakes to characterize the fate of Hg in one such plant.

2. Experimental

2.1. TREATMENT PLANT DESCRIPTION

Sampling and analysis of total Hg concentrations in major process streams were carried out at the Metropolitan Wastewater Treatment (Metro) Plant in St. Paul, Minnesota. The Metro Plant utilizes primary and activated sludge secondary treatment to process 10.0 m³/s of wastewater from the metropolitan Minneapolis-St. Paul area. Wastewater flow through the plant is divided between east and west treatment trains, the larger east primary process treating approximately 70% of the daily flow. Flow equalization prior to secondary treatment results in approximately equal hydraulic loadings on the east and west activated sludge/final clarification process units. Residual primary and thermally conditioned waste activated sludges are dewatered and incinerated in six multiple hearth incinerators. Emissions from the incinerators are controlled with high temperature quad cyclones, and venturi and packed tower wet scrubbers, in series. Spent scrubber water is returned to the secondary influent stream for treatment. A simplified diagram of the Metro Plant process flow scheme is shown in Figure 1.

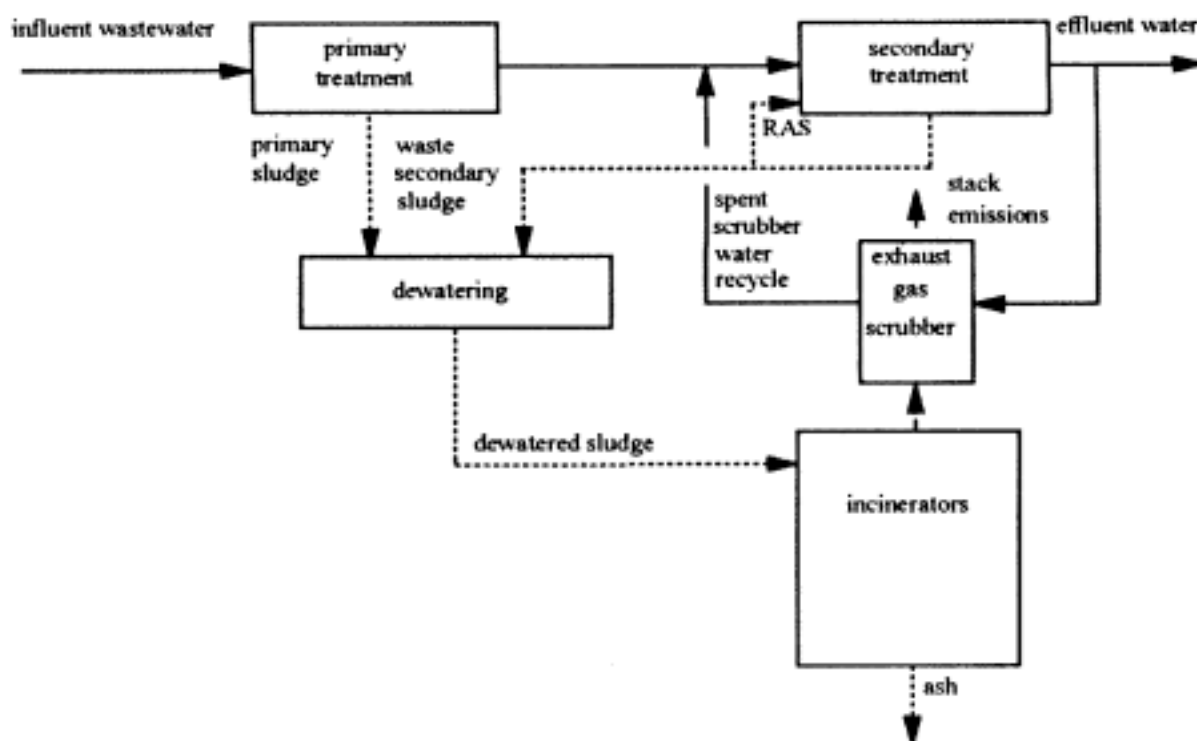


Figure 1. Simplified Metro Plant process flow scheme.

2.2. WASTEWATER AND SLUDGE SAMPLING PROCEDURES

Sampling of major process streams was carried out over a nine week period during which grab samples were collected every third day. Sampling times were randomized to provide a representative picture of daily Hg loadings. Over 200 samples from major target streams were collected and analyzed. Targeted streams were: east primary influent, effluent, and sludge; west primary influent and effluent; east secondary influent, effluent, and waste activated sludge; west secondary influent, effluent, and waste activated sludge; and spent incinerator exhaust scrubber water.

Samples were collected using a modification of the "clean hands/dirty hands" two-person sampling technique (Brooks Rand, 1990). Wastewater samples were collected from open process streams by having the "clean hands" member of the sampling team discard the preservation solution and place the 500 ml Teflon sample bottle on the end of an acid-soaked polyethylene sampling stick, which the "dirty hands" member then placed in the process stream, with the bottle opening about 15 to 30 cm below the water surface. The bottle was rinsed once with sample water, filled again, then "clean hands" capped the bottle tightly, removed it from the sampling stick, and placed it back into its original double zip-lock bags. Samples collected from process weirs were obtained similarly, except that "dirty hands" held the sampling stick so that the bottle opening was placed in the falling nappe of the weir discharge. Liquid activated sludge samples were collected from continuous-flow sampling sinks by having "clean hands" dip the bottle into the flowing stream. Liquid primary sludge samples were collected from a sampling tap which was flushed thoroughly before sampling. Here, "clean hands" held the sample bottle in the flowing stream. Spent scrubber water samples were collected from a sampling tap in the same manner as the primary sludge samples.

2.3. INCINERATOR EXHAUST GAS SAMPLING PROCEDURE

Total Hg in the incinerator exhaust gas was sampled using iodated carbon traps (Metzger and Braun, 1987; Bloom, 1993). The sampling train consisted of, in series, a front trap, a backup trap, Teflon tubing, a silica gel impinger, a dry gas meter and a vacuum pump (see Figure 2). Connections between the traps and the tubing were made with acid-leached Teflon friction-fit connectors. A 112 cm piece of 6.35 mm OD stainless steel tubing was used for support of the in-stack sample train elements (traps and tubing). The function of the metal tubing was for support only; Hg in the sample gas came in contact only with the inside of the traps. The iodated carbon traps (MSA #459003) were affixed to the support so as to point into the sample flow. Samples were collected at 200 ml/min for 50 minutes. The sampling point was downstream of all emissions control equipment. At the end of the sampling period, the pump was turned off, and the probe (traps and Teflon tubing secured to stainless tubing) was removed from the stack sampling port. The front and backup traps were removed, capped individually with plastic caps, and labeled. They were placed in zip-lock bags and immediately transported to the clean analytical laboratory for processing. Ten sampling runs were made, and four of the six incinerators were tested. On seven sampling runs, historical incinerator air flowrate data were used to calculate Hg mass loadings. On the other three sampling runs, flowrate data obtained by pitot tube measurements at the time of the test were used. The two methods of mass loading calculation yielded similar results.

2.4. ANALYTICAL REAGENTS AND LABORATORY PROCEDURES

Bromine monochloride reagent was prepared by carefully adding, first, 5.4 g of KBr, and then, one hour later, 7.6 g of KBrO_3 to 500 ml of low-Hg HCl in a stirred Teflon bottle. A 5% potassium permanganate solution was prepared by adding 5 g of KMnO_4 to 100 ml of ASTM Type I water (DDW). A 5% potassium persulfate solution was prepared by adding 5 g of $\text{K}_2\text{S}_2\text{O}_8$ to 100 ml of DDW. Stannous chloride reagent was prepared by adding 20 g of SnCl_2 to 10 ml of low-Hg HCl, then diluting to 100 ml with DDW; this reagent was then purged for one hour with Hg-free nitrogen at approximately 250 ml/min. Hydroxylamine hydrochloride solution was prepared by adding 30 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$ to 100 ml of DDW; this solution was purged overnight with Hg-free nitrogen at approximately 250 ml/min. All reagents were prepared weekly, except for hydroxylamine hydrochloride, which was prepared monthly, and stannous chloride, which was prepared daily. Concentrated nitric and sulfuric acids were used as received.

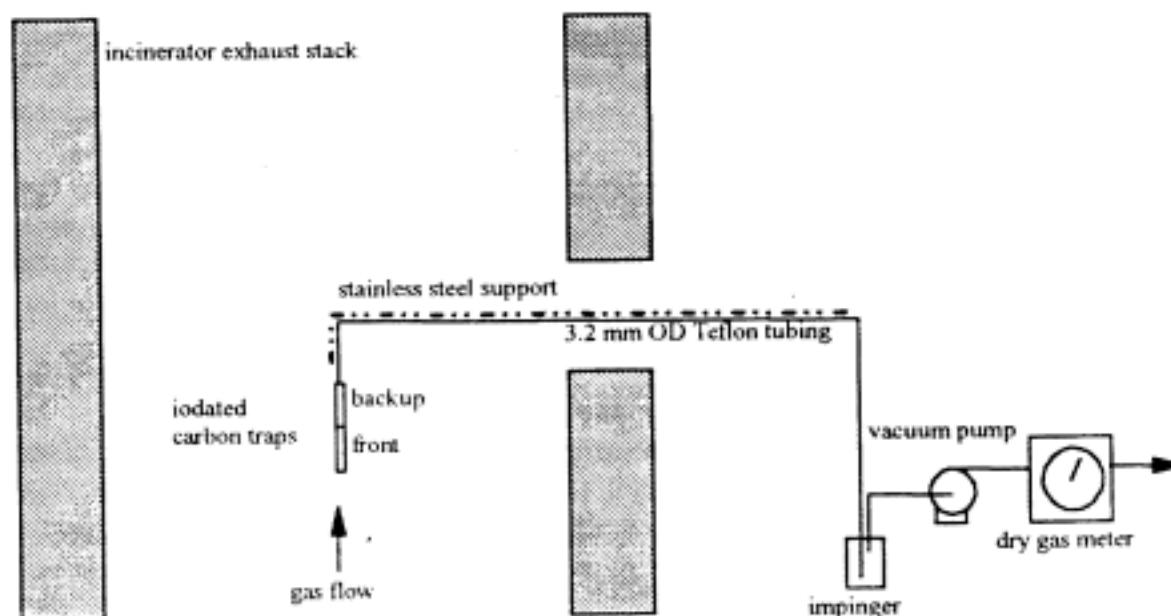


Figure 2. Incinerator exhaust gas sampling train.

New 500 ml Teflon FEP bottles and 30 and 60 ml Teflon FEP vials used in this study were first acid-leached in concentrated nitric acid at 60°C for six days. They were rinsed thoroughly with DDW, then filled with 1% HCl and placed in an oven at 60°C overnight. Following another thorough rinsing with DDW, the bottles and vials were filled once more with 1% HCl, capped tightly, then left in a class 100 HEPA-filtered clean air hood to dry, before being double-bagged with new polyethylene zip-lock bags. The bottles and vials were stored in plastic buckets in the clean analytical laboratory until use.

Following their use, the bottles and vials were rinsed, in succession, with tap water, nitric acid, chloroform, and then tap water again, before being placed in concentrated nitric acid at 60°C for three days of acid leaching. Sample bottles in which the acid permanganate digestion was carried out were pre-rinsed with hydroxylamine hydrochloride solution prior to the rinsing scheme above. Following the acid leaching, the bottles and vials were rinsed with DDW, filled with 1% HCl, left overnight at 60°C, rinsed again, filled with 1% HCl, then double-bagged and stored until further use.

A record of the sampling history of each 500 ml bottle was maintained, and individual bottles were dedicated for use on particular process streams. Bottles used for sampling high concentration streams were not used later for low concentration streams. This, along with the rigorous cleaning program, helped to assure the integrity of the collected samples.

2.5. SAMPLE DIGESTION PROCEDURES

After sampling, the double-bagged samples were immediately placed in a cooler, and transported within one hour to the clean analytical laboratory for processing. Once there, the bottles were removed from their bags, rinsed externally with DDW, and placed in the class 100 clean air hood. For wastewater samples, digestion reagents were added directly to the sample bottles, and the bottles double-bagged with new bags. Samples were allowed to sit overnight in the clean room hood, or in a clean plastic bucket. The next day, single-bagged and tightly capped sample bottles were placed in a convection oven at 95°C for two hours. Digestion reagents for various wastewater samples are described in Table I.

TABLE I

Sample digestion methods

sample type	digestion method
primary influent	150 ml/L KMnO_4 , etc. [†]
primary effluent	60 ml/L BrCl ; 2 hrs at 95°C
secondary influent	150 ml/L KMnO_4 , etc. [†]
secondary effluent	20 ml/L BrCl ; 2 hrs at 95°C
spent incinerator exhaust scrubber water	60 ml/L BrCl ; 2 hrs at 95°C

[†] 150 ml/L KMnO_4 , 80 ml/L $\text{K}_2\text{S}_2\text{O}_8$, 50 ml/L H_2SO_4 , 25 ml/L HNO_3 ; 2 hrs at 95°C

Sludge samples were digested differently than wastewater samples. Three-ml aliquots were pipetted into 30 or 60 ml Teflon FEP vials. One-half ml of HCl was added, followed by 3 ml of concentrated sulfuric acid and 7 ml of concentrated nitric acid. The vials were capped tightly and left to sit, double-bagged, overnight in the clean air hood. The next day, 10 ml of the digestion liquor was pipetted into an acid-leached 100 ml volumetric flask. The flask was placed in sand on a hot plate at 250°C for 2-3 hours or until the dark orange-red color had faded. An acid-cleaned 1-inch glass marble was placed atop the flask to minimize air exchange, promote refluxing and relieve pressure buildup. Digested

samples were diluted to 100 ml with 0.5% bromine monochloride solution.

The iodated carbon traps from the incinerator exhaust gas sampling were prepared for analysis by transferring the iodated carbon and cloth particulate filter from the trap to a 30 ml Teflon vial. Two mls of concentrated sulfuric acid and 5 mls of concentrated nitric acid were then added, the vials were capped tightly, double-bagged and left in the clean air hood overnight. The next day, the samples were placed in a convection oven at 110°C for 3 hours (Bloom, 1994). After cooling, the samples were diluted by the addition of 7 mls of DDW.

2.6. ANALYTICAL PROCEDURES

Aliquots of the digested samples were analyzed using the cold vapor atomic fluorescence technique with dual-trap gold amalgamation (Fitzgerald and Gill, 1979; Brooks Rand, 1990). Samples treated with acid-permanganate or bromine monochloride were prereduced with hydroxylamine hydrochloride. For analysis, a sample aliquot was pipetted into the 250 ml cold vapor bubbler containing approximately 150 ml of DDW and one ml of stannous chloride reagent. Samples were purged for 15 minutes with gold-filtered nitrogen at 250 ml/min. The purged mercury was collected on a gold-coated quartz sand trap (Brooks Rand AF-20). A soda-lime (Mallinckrodt Mallcosorb) acid/moisture pre-trap was used between the bubbler and the gold trap to minimize acid/moisture effects on the gold-coated sand. This procedure was carried out entirely within a clean air hood.

Following the collection of the Hg on the gold trap, the trap was placed in a NiCr coil and heated to 450-500°C for three minutes while under gold-filtered helium flow of 30 ml/min. The desorbed Hg was collected on an analytical gold trap. The analytical trap was subsequently heated similarly, the Hg and carrier gas thus entering the atomic fluorescence detector (Brooks Rand Model CVAFS-2). The detector signal was recorded and integrated with an HP 3395 Integrator. Peak area was used in all calculations.

In addition to frequent calibration checks (at least every six samples), the quality of the data was assured with the daily analysis of NIST 1641c Mercury in Water SRM. The average of twenty daily determinations of this SRM was 1.46 +/- 0.03 µg/ml; the certified value is 1.47 +/- 0.04 µg/ml.

3. Results and Discussion

The measured process stream Hg concentrations were combined with flowrate data to calculate process stream Hg loadings throughout the Metro Plant. Mass balances across individual processes and across the entire plant were evaluated according to the equation

$$\text{mass in} - \text{mass out} = \text{balance}$$

where "balance" represented the mass of Hg found to be either in excess or unaccounted for. Dividing the "balance" by the "mass in" gave a relative measure of the mass imbalance observed. The results of balance calculations performed for the east primary

and east and west secondary processes at the Metro Plant are shown in Table II. No balance was calculated for the west primary process as no sludge samples were taken there. The balance term in Table II is given as a percentage of the influent mass.

The Hg balance across the east primary process showed approximately 11% more Hg coming out than going in. A probable explanation for the excess Hg found leaving this process is the overestimation of the primary sludge Hg loading. Primary sludge stream solids levels vary widely and unpredictably over time, leading to difficulty in getting a representative sample. Plant process monitoring records indicated that the average total suspended solids (TSS) concentration in this stream over the sampling program duration was approximately 6200 mg/L. The average TSS concentration measured in our sampling was approximately 7500 mg/L, or 21% higher. The primary sludge Hg concentration was highly correlated (99% significance level) with the TSS concentration, and the oversampling of solids in this stream resulted in the overestimation of the Hg concentration and loading.

TABLE II

Mass loadings (g/day) and balance values for Metro Plant treatment processes

	influent	effluent	sludge	balance (%)
east primary	171	36	154	-11
east secondary	92	3	83	7
west secondary	160	6	135	12

The average Hg removal in the east primary treatment process was 79%, while total suspended solids removal (average: 71%) and volatile suspended solids removal (average 70%) were somewhat lower. Previous studies have reported that more than 90% of the Hg in raw municipal wastewater is typically associated with particulate phases (Oliver and Cosgrove, 1974; Goldstone *et al.*, 1990), and work in our lab has indicated that approximately 85% of the Hg in Metro Plant primary influent is associated with particle sizes greater than 5 μm . This association with solids accounts for the relatively good Hg removal observed in primary sedimentation processes (Goldstone *et al.*, 1990).

Mercury mass balances across the east and west secondary processes at the Metro Plant come reasonably close to closure. The east side balances within 7%, while the west side result shows 12% more Hg going in than coming out. In part, these discrepancies are thought to be due to overestimation of the secondary influent flowrates, and, thus, the influent loadings. Secondary solids and flow imbalances have previously raised questions about the accuracy of secondary influent and sludge flow metering at the Metro Plant (Tetreault, 1994), and metering accuracy is currently under study. Further evidence suggesting overestimation of the secondary influent loading is that the total primary effluent (67 g/day) and spent scrubber water (153 g/day) Hg loadings do not add up to the

estimated total secondary loading of 252 g/day. These data would suggest that the estimated total secondary influent loading is high by approximately 10 to 15%.

The west secondary influent Hg loading is, on average, 74% higher than that on the east side (160 vs 92 g/day). This is because the heavily-loaded spent scrubber water ordinarily goes to the west side. Effluent and waste activated sludge Hg loadings on the west side are similarly elevated, reflecting the higher inputs.

The Hg loadings of all major process streams are shown on the simplified process flow diagram in Figure 3. Here, east and west side loadings are combined to give overall primary and overall secondary process loadings. The primary sludge mass loading is shown in parentheses to indicate that this value was calculated by difference (balance assumed to equal 0) rather than by direct measurement. Similarly, the dewatered sludge mass loading was calculated by adding the primary and waste activated sludge loadings together.

The Hg balance around the entire treatment plant closed within 2% (balance/mass in < 2%), a good result given the difficulties and variability inherent in such exercises (Goldstone and Lester, 1991). Of the 248 g/day entering the Metro Plant, more than 95% (241 g/day) is estimated to be emitted to the air via incinerator emissions, while only 4% (10 g/day) is discharged to the Mississippi River via the effluent stream. Based on measurements made previously, the incinerator ash stream accounted for negligible Hg output from the plant. The volatilization of Hg species in wastewater treatment processes

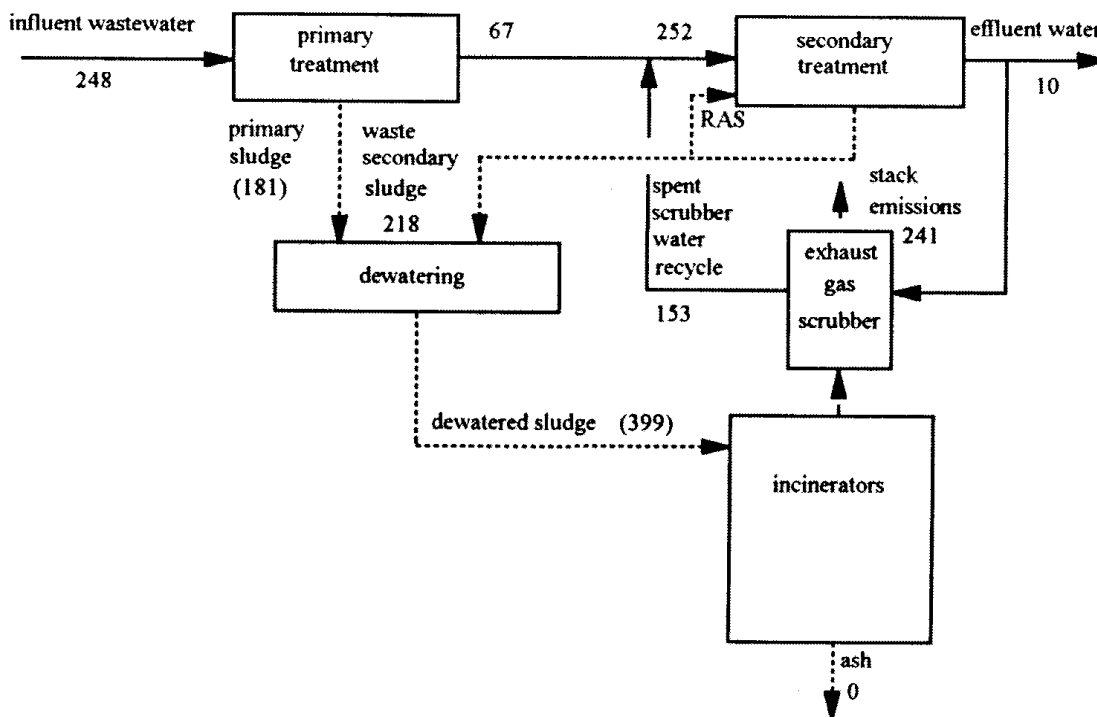


Figure 3. Metro Plant mercury mass flows, grams/day.

(Goldstone *et al.*, 1990) is also apparently of negligible significance at the Metro Plant. Because of the preferential association of Hg with solids, the Metro Plant is very effective in removing Hg from the wastewater stream; however, the incineration process is not effective in controlling or containing the Hg removed.

The difficulty in controlling Hg discharges from the Metro Plant stems from the recycle of the spent scrubber water stream. The scrubbers remove approximately 40% of the Hg mass from the incinerator exhaust stream. That mass is returned to the secondary treatment process, where it associates once more with sludge solids, and returns to the incinerators. The cycle repeats, and the Hg has multiple opportunities to escape the scrubber, until, eventually, it does. A similar situation has been observed for cadmium (Cd) at the Metro Plant; however, because some Cd partitions to the residual ash, all of it is not lost out the stack. This recycle arrangement results in elevated sludge Hg loadings and elevated loadings in all secondary treatment process streams, including the effluent. Both atmospheric emissions and effluent discharges could be reduced by treating the spent scrubber water outside of the wastewater treatment process, that is by not sending it back into secondary treatment, but by handling it elsewhere. A novel sulfide precipitation process designed to remove Cd from spent scrubber water was piloted at the Metro Plant and shown to provide removal of over 90% of the Cd and over 70% of the Hg in this stream (MWCC, 1991); process optimization would likely yield higher Hg removal values. This is one way in which internal Hg loadings and environmental Hg discharges at the Metro Plant might be reduced. Alternatively, a non-water-based emissions control process (activated carbon injection, for instance (EPA, 1992)) could be employed, where the Hg removed from the exhaust stream would be handled outside of the wastewater treatment process.

Metro Plant incineration operations are fairly typical of the industry in the United States. Multiple hearth incinerators and wet scrubber emissions control equipment are normally employed, and the internal recycle and treatment of spent scrubber water is typical (EPA, 1985; EPA, 1990). Thus, it could be expected that other wastewater treatment plants incinerating sewage sludge might display similar process Hg dynamics.

4. Conclusion

Almost all of the Hg entering a large municipal wastewater treatment plant was found to be emitted to the atmosphere via sewage sludge incineration exhaust. While the plant achieved excellent removal of Hg from the wastewater stream, the handling of the residual sludge solids resulted in the loss of that Hg to the atmosphere.

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